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Investigation of UV Polymerized Fullerene Nano Whisker by ESR and FET Characteristics

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1. Introduction

Fullerenes have been proposed for near future applications for high performance n-type organic field effect transistors (FETs). However, their inability to operate under ambient atmosphere has prevented fullerenes from being applied to electronic devices. Since the first report in 1993 [1], several trials, such as polymerization due to UV irradiation, have been proposed. In case of UV irradiated thin film of C_{60}, we have previously observe FET performance in atmosphere [2].

It is well known that single crystalline organic semiconducting materials indicate good performance for applying to FET devices, such as high mobility and high on/off ratio [3]. It is important that we use single crystalline semiconductors for a development of high performance organic FETs. A novel crystal glows method was developed by Miyazawa and coworkers which is called liquid liquid interfacial precipitation (LLIP) method [4].

In this study, we focus on fullerene nano whisker (FNW), which are fine crystalline wires consisting of C_{60}. FNWs are fabricated by the LLIP method based upon the system of C_{60} saturated m-xylene and isopropyl alcohol. FNWs have a number of attractive features, such as their high aspect ratio, nano scale semiconductor crystal structure, n-type organic semiconductor behavior, and their fabrication by liquid process. The electron transport properties of FNW-FETs have been studied by observing n-type FET characteristics. However, as in the case of C_{60} thin film FETs, it is difficult to achieve FNW-FET operation in atmosphere. Therefore, we have performed UV irradiation of FNW-FETs. In the case of a photo irradiation of FNWs, it has been reported that FNW was easily polymerized by intense laser irradiation [5]. We investigate UV polymerized FNW by use of observing FET characteristics and ESR in broth ambient atmosphere and high vacuum.

2. Experiments and results

Preparation of FNWs

We prepared FNWs as following LLIP method. Fig.1 shows SEM image of the prepared FNWs on SiO_2 substrate. The diameter and length of FNW are typically 500 nm and more than 10 μm respectively.

Investigation of FET characteristics

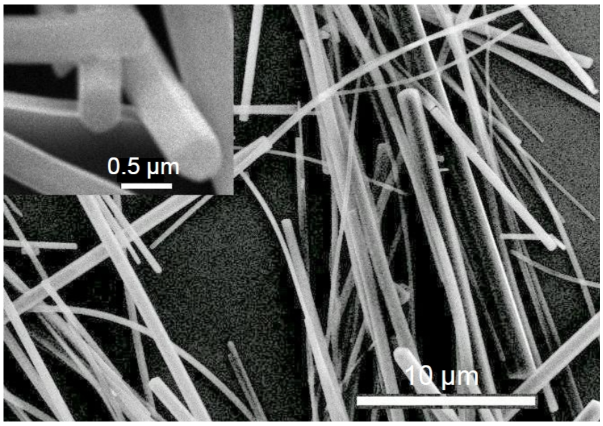

Fig. 1 SEM image of prepared FNWs on SiO_2 substrate

In this study, our FNW-FET was fabricated with a bottom contact configuration because in our previous research on thin film C_{60}, it was clarified that the top-contact electrodes blocked off the UV-light and obstructed polymerization underneath the electrodes. In this, the fabricated FNW-FET has two Au / Ti (20 nm / 10 nm thickness, respectively) electrodes as source and drain on a SiO_2 / Si substrate, allowing the use of the heavily doped silicon as a gate electrode, SiO_2 (600 nm thickness) insulator layer. The electrode distance and width were 40 μm and 0.5~1 mm respectively. It is noted that the electrode width isn't important because real channel width is deiced by the number of bridging FNWs and them diameter. The width of electrode decide only the number of bridging FNWs. We obtained FNW-FETs in which several FNWs bridge the two (source and drain) electrodes.

The UV irradiation involved a procedure in which (1) FNW-FET was annealed in vacuum at 440 K before UV irradiation, (2) The substrate temperature was fixed at 300 K, (3) The wavelength of irradiated UV light is selected by use of a short path filter in order to cut off wavelength longer than 400 nm. The UV polymerized FNW-FETs show clear FET *IV* characteristics in vacuum (~10^{-5} Pa). The value of μ_{FE} has estimated from transconductance g_m and is decreased by one order of magnitude due to UV irradiation. At the same time, the threshold voltage V_{TH} was drastically lowered from -1 to -40 V. Moreover, we have investigated the effect of atmospheric exposure on the UV polymerized FNW-FET by introducing air into the measurement chamber. Fig.1 shows transfer characteristics of same device of (a) before UV irradiation in vacuum, (b) after UV irradiation in vacuum, and (c) after UV irradiation in atmosphere for four hours. These result indicate that UV polymerized FNW-FET can work even under ambient atmosphere.

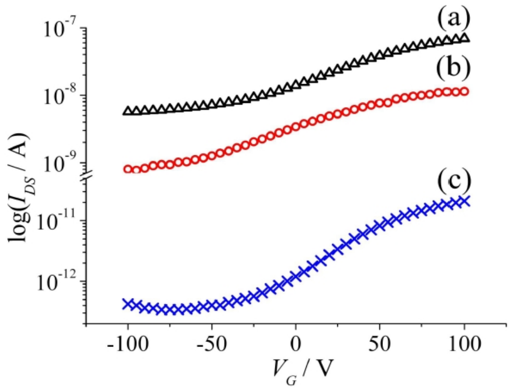

Fig. 2 Transfer characteristics of (a) pristine FNW-FET, (b) UV polymerized FNW-FET, (c) UV polymerized FNW-FET in ambient atmosphere

Investigation of spin in polymerized FNW by use of ESR

We have studied the charier behavior of UV irradiated FNW in ambient atmosphere by use of ESR. The measured sample is exposed in atmosphere after UV irradiation at several weeks. A obtained differentiation resonance line shape was a Lorentz type line shape, and *g* value was estimated at 2.0026. Fig. 3 shows a temperature dependence of peak-to-peak line width of pristine FNW and polymerized FNW. We observed two differences, (1) peak-to-peak width of polymerized FNW (lower) independent on temperature, in the other hand peak-to-peak width of pristine FNW almost depend on temperature, (2) peak-to peak width of irradiated FNW at room temperature is bigger than peak-to-peak width of pristine FNW. These results indicate that UV irradiated FNW is much closer to metallic in compared with pristine FNW.

Fig. 4 shows that the spin number ratio $\{(N_S^{UVFNW})^{-1}/(N_S^{FNW})^{-1}\}$ decreases as temperature increase. The temperature dependence of $(N_S^{UVFNW})^{-1}/(N_S^{FNW})^{-1}$ indicate the temperature dependence of magnetic susceptibility ratio. $\chi^{UV\text{-}FNW}$ shows a weaker dependence on temperature and $\chi^{UV\text{-}FNW}$ is much closer to Pauli magnetic susceptibility. These results was induced by reduction of energy of bandgap due to polymerization.

3. Conclusions

We have studied on UV polymerized FNW-FET which remain to perform in air. We suggest a clear change of FET parameter due to UV irradiation and air exposure, it is related to reduction of energy of band gap. The results of electron transport qualitatively correspond with ESR results which FNW polymer is closer to metallic.

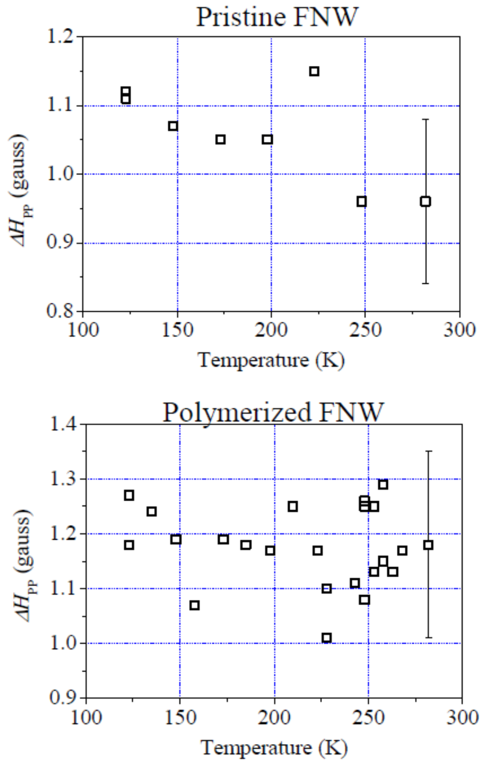

Fig. 3 Temperature dependence of peak-to-peak width of pristine FNW (upper) and polymerized FNW (lower)

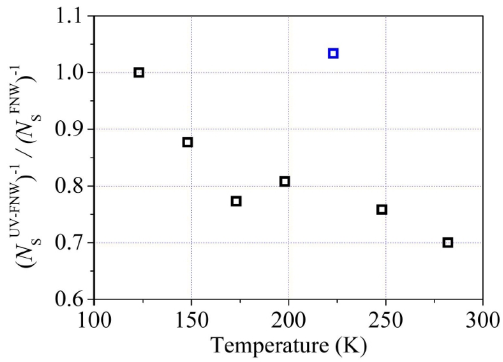

Fig. 4 Temperature dependence of spin number ratio of pristine and polymerized FNW

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